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Fate of Fenthion in Salt-Marsh Environments: 2 Transport and Biodegradation in Microcosms

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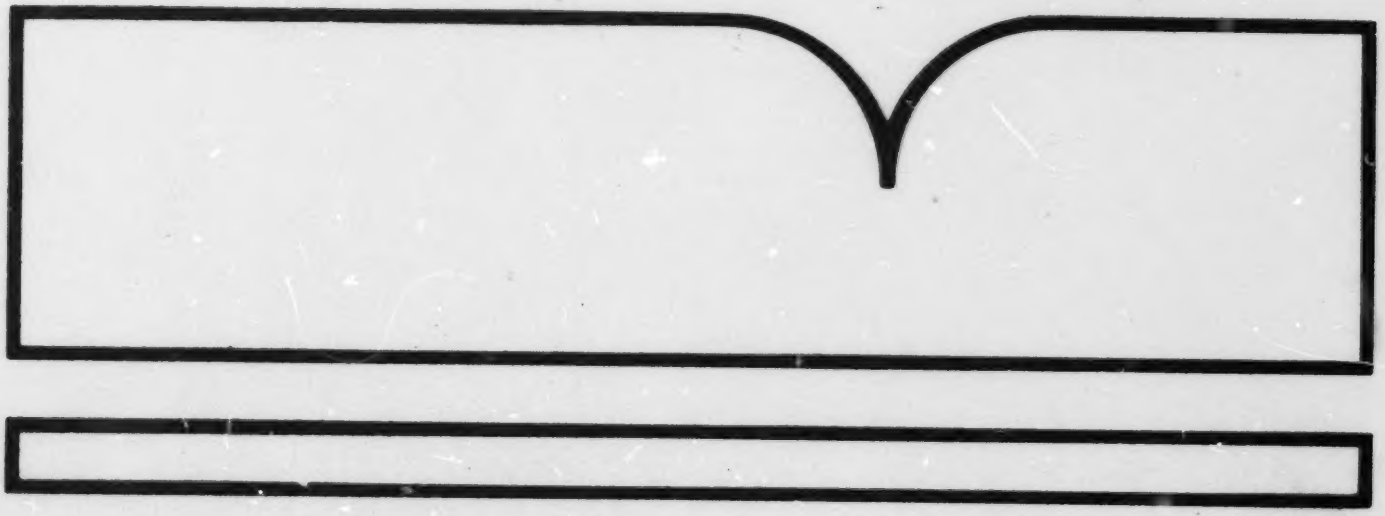

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16. ABSTRACT

The fate of fenthion was examined in microcosms to define the possible interaction between sediment and biodegradation in the field. A mathematical model was also calibrated to calculate the distribution of fenthion in microcosms. Intact sediment cores, both with and without Juncus roemerianus, were removed from a salt marsh and placed into microcosm vessels to simulate the undisturbed sediment bed of a salt marsh and the areas containing Juncus. In formalin-sterilized microcosms without plants, fenthion disappeared exponentially from the water column with a half-life of 105.0 h. Fenthion had a half-life of 35.5 h in the microcosm without plants. In microcosm with plants, the half-life was slightly faster (33.2 h). In fractionated sediment cores, fenthion was found at greater depths in nonsterile systems than predicted by diffusion and sorption in sterile microcosms, possibly because of bioturbation. Distribution of fenthion in sediment was not appreciably different between microcosms with and without plants. Fenthion appeared to be biodegraded in upper (1 to 7 mm) sediment layers.

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FATE OF FENTHION IN SALT-MARSH ENVIRONMENTS: II. TRANSPORT AND BIODEGRADATION IN MICROCOSMS

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Abstract—The fate of fenthion was examined in laboratory microcosms to describe interaction between sediment and biodegradation in the field. A mathematical model also was calibrated to calculate distribution of fenthion in microcosms. Intact sediment cores, with and without a salt-marsh plant, *Juncus roemerianus* (black needlerush), were placed in microcosm vessels to simulate an undisturbed sediment bed of a salt marsh and areas containing *Juncus*. In a formalin-sterilized microcosm without plants, fenthion disappeared exponentially from the water column with a half-life of 105.0 h. Fenthion had a half-life of 35.5 h in a nonsterile microcosm without plants. In the nonsterile microcosm with plants, the half-life was slightly shorter, 33.2 h. The sediment was fractionated into 0.5 cm layers. Fenthion was found at greater sediment depths in nonsterile systems than predicted by diffusion and sorption in the sterile microcosm, possibly because of bioturbation. Distribution of fenthion in sediment was not appreciably different between microcosms with and without plants. Fenthion appeared to be biodegraded in the upper (1 to 7 mm) sediment layers.

Keywords—Fenthion Microcosm Biodegradation Bioturbation Model

INTRODUCTION

Several studies have shown that biodegradation rates of many xenobiotic chemicals increase in the presence of sediment [1–4]. In contrast, Steen et al. [5] have shown that chemicals sorbed to sediment surfaces are not available for degradation and degradation rates are reduced with increasing sediment concentrations. Plants provide surfaces for microbial attachment [6,7], and continually release dissolved organic compounds that could support a large microbial biomass [8–14]. The interaction between plant and microbial communities presents a unique ecological situation where microbial activities may have a significant effect on the fate of xenobiotic chemicals. In addition, O'Neill et al. [15] and Drifmeyer [16] showed that leaves provide surfaces for adsorption of xenobiotic chemicals.

Pritchard and Bourquin [3] have suggested that microcosms containing an intact, relatively undisturbed core of sediment can provide an excellent method for studying various aspects of biodegradation processes. Our study examined the significance of microbial populations associated with undisturbed sediment surfaces, bioturbation, and the presence of plants in determining the fate of fenthion in a microcosm system representative of a salt-marsh environment. Fenthion is used as a mosquito control agent in salt-marsh areas and consequently is a potential contaminant of marsh grasses and sediment. Because fenthion is bio-

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degradable [17,18], it is an ideal chemical to test the effects of bacteria associated with plants and sediment on biodegradation processes.

MATERIALS AND METHODS

Chemicals

Fenthion (O,O-dimethyl-O-[4-(methylthio)-*m*-tolyl]-phosphorothioate) (97.2% pure) was obtained from the U.S. EPA Pesticides and Industrial Chemicals Repository (Research Triangle Park, NC).

Microcosms

Water (salinity = 11‰) and sediment samples were collected from a salt marsh on Santa Rosa Island (Eglin Air Force Base, near Fort Walton Beach, FL). Sediment cores with plants, *Juncus roemerianus*, and without plants were collected from the margin of the marsh with a cylindrical, clear acrylic corer (56 cm × 12.5 cm) to a depth of 7.0 cm. A sediment–plant core contained 20 emergent leaves. The cores with water from the marsh were transferred in the field to 4-liter (13.4-cm diameter) glass vessels (reaction flask body, Corning Glass Co., Corning, NY). At the laboratory, water was siphoned from each vessel and replaced with 2,500 ml of water collected from the marsh. The systems were operated statically (no flow-through conditions). A light:dark cycle (12 h:12 h) was provided by cool white 40-W fluorescent bulbs at an intensity of 260 lux. The outer surface of the vessels had been painted black at the sediment line to exclude light penetration below the sediment interface. The microcosms were partially submerged in a plexiglass water bath maintained at 20°C by a Neslab RTE-4 refrigerated circulating bath (Neslab Instrument Co., Portsmouth, NH). Dissolved oxygen, temperature, and pH were measured daily to monitor system stability. *Juncus* leaves grew 0.8 to 0.95 cm during the 8-d experiment, indicating that plants probably were not stressed by experimental conditions.

There were three different microcosm treatments: sterile without plants, nonsterile without plants, and nonsterile with plants. A microcosm without plants was sterilized with formalin (final concentration 5% [v/v]) 4 d prior to addition of fenthion. The sterility of water in the microcosm was verified by standard agar plating techniques.

An acetone solution (10 ml) containing 500 μg fenthion was added to the 2.5 liters of water in each microcosm to produce a nominal concentration of 200 μg fenthion per liter. Duplicate water samples were taken from each microcosm at 3 h, 6 h and daily thereafter. Duplicate water samples were averaged for graph presentation.

Sample analysis

Hexane (10 ml) was added to 10-ml water samples and samples were rotated for 1 min to extract fenthion. The sample was then centrifuged for 5 min at 700 *g* (Damon International Model K, Boston, MA) to break up emulsions. Fenthion in the hexane extract was quantified with a gas chromatograph (helium carrier gas, 30 ml/min, column oven 200°C, injector temperature 220°C) equipped with a nitrogen–phosphorous detector and a 0.75% SP2250/0.97% SP2401 column (100/120 mesh, 6 ft, 2 mm i.d., Supelco, Inc., Bellefonte, PA).

At the end of the experiment (190 h), water was siphoned from each vessel without disturbing the sediment surface. Leaves from all plants were severed at the sediment surface and frozen for fenthion residue analysis. For extraction, the leaves were cut into 2-mm pieces, suspended in water and ground with a Polytron (Brinkman Instruments, Westburg, NY) for 3 min. A 10-g portion of the plant–water slurry was mixed with 10 ml acetonitrile, ground as described above and centrifuged 5 min at 600 *g*. The supernatant was removed and the sample was extracted twice more with 5 ml acetonitrile and a polytron. Extracts were combined with 70 ml of aqueous 2% sodium sulfate. The resulting solution was extracted three times with 10 ml hexane and extracts were combined, concentrated, and analyzed by gas chromatography.

After water was siphoned from each vessel, a chrome-plated brass tube (3.7 cm i.d. × 9.0 cm length; 0.5 mm wall thickness) was inserted vertically into the undisturbed sediment bed of each microcosm; then the microcosm vessels and contents were frozen. The frozen sediment core was removed by warming the exterior of the vessel under hot tap water. The metal tube and its contents were separated from the surrounding sediment and refrozen. Microcosm vessels were rinsed with acetone or acetonitrile to remove and quantify residual fenthion.

The sediment was fractionated and processed to determine the concentration of extractable fenthion in the sediment and interstitial water. Frozen sediment in the brass tubes was mechanically extruded and sliced into 0.5-cm layers with a sharpened spatula. Sections were collected on foil trays, rinsed into centrifuge tubes with 5 to 10 ml acetonitrile, vigorously shaken for 2 min, and centrifuged for 5 min at 700 *g*. The supernatant was decanted and the extraction repeated. Combined extracts were

added to 70 ml 2% aqueous sodium sulfate, back-extracted twice with 10 ml hexane, and concentrated to 10 ml. Separate sediment samples were spiked with 100 μg/L of fenthion, frozen and extracted as above to determine recoveries after freezing. Fenthion residues in sediment were expressed in the same units as predicted by the mathematical model: microgram fenthion per liter of sediment layer.

Recoveries from spiked water and sediment samples were 84 and 79%, respectively. The water and sediment samples were corrected to 100% to compare these observations with predictions from a mathematical model.

After extraction, sediments were dried (105°C) to a constant weight. Sediment moisture content was calculated from differences between wet and dry sediment weights and the interstitial water volume decanted after centrifugation. Total volume of interstitial water was divided by the volume of the sediment layer to calculate porosity. The sediment was combusted (550°C) and sieved through a 63-μm screen to determine sand content [19]. For comparisons with shake-flask tests [17], detritus was considered to consist of all sediment, excluding sand, and was calculated for each sediment layer by subtracting dry weight of sand from total sediment dry weight.

A SAS (Statistical Analysis System, SAS Institute, Cary, NC) regression analysis was used to determine first-order rate constants for loss of fenthion from the water column in microcosms. The F statistic was used to test significance of the regression. A SAS general linear model procedure compared the rate constants between the microcosms.

RESULTS

Loss of fenthion from the water column in all three treatments conformed to first-order kinetics (Figs. 1-3). First-order rate constants, estimated from data points between 2 h (to allow complete water-column mixing) and 190 h, were -0.0195 h^{-1} in nonsterile microcosms without plants and -0.0209 h^{-1} in nonsterile microcosms with plants ($r^2 > 0.98$). The difference in rates was not significant ($p = 0.2655$). The decay constant in the sterile microcosm was -0.0066 h^{-1} ($r^2 = 0.98$) and was significantly different from rates in both nonsterile microcosms ($p = 0.0001$).

Sediment composition in the sterile microcosm and nonsterile microcosms with and without plants is shown in Table 1. The sand content, indicative of porosity, changed with depth.

Fenthion concentrations in different sediment layers of nonsterile microcosms with and without plants and in the sterile microcosm are shown in Figures 4, 5 and 6. Fenthion was found in sediment to depths of approximately 5.5 cm in nonsterile microcosms and approximately 2.5 cm in the sterile microcosm. The top 0.5 cm sediment layer in the microcosm containing *Juncus* plants had a higher fenthion concentration than the nonsterile microcosm without plants.

A budget of fenthion from all microcosms is shown in Table 2. Microcosm vessel rinses accounted for less than 1% of the total fenthion added to the systems. Emergent plant leaves accounted for ap-

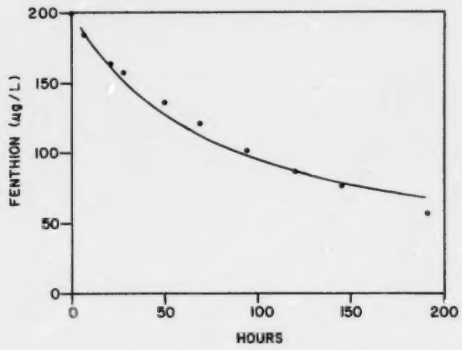

Fig. 1. Observed (circles) and predicted concentrations (solid line) of fenthion in the water of a sterile microcosm. Model input data are listed in Table 3.

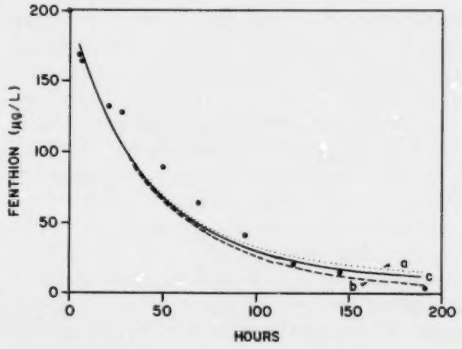

Fig. 2. Observed (circles) and predicted concentrations of fenthion in the water of a nonsterile microcosm without plants. Model predictions of fenthion distribution using data listed in Table 3 were based on three adjustments in the sediment biodegradation rate constant: (a) zero biodegradation; (b) biodegradation throughout the sediment; (c) biodegradation limited to the top 7 mm of sediment.

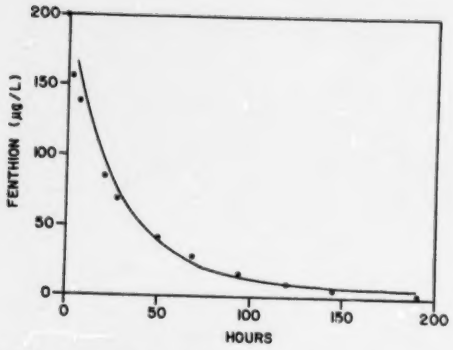

Fig. 3. Observed (circles) and predicted concentrations (solid line) of fenthion in the water of a nonsterile microcosm with plants. Model input data are listed in Table 3.

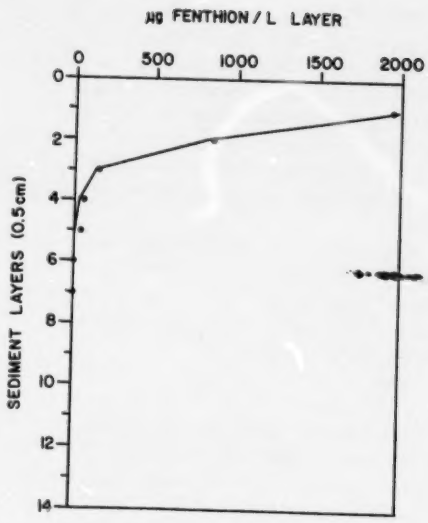

Fig. 4. Observed (circles) and predicted concentrations (solid line) of fenthion in the sediment of a sterile microcosm. Model input data are listed in Table 3.

proximately 1% of total fenthion added to the system. The association of fenthion with plants was not distinguished between uptake or adsorption to plant surfaces.

Worm burrows and mounds were obvious in the nonsterile microcosms throughout our study. Results of the invertebrate activities were evidenced by the increased porosity values in the nonsterile microcosms as compared to the sterile microcosm (Table 1). High porosity values in the top sediment layers reflected lack of sand and relatively small amounts of flocculent detritus resulting in displacement of only minute volumes of water; thus the volume was almost totally water. In the lower sediment depths of the microcosm with plants, roots and rhizomes functionally appeared as detritus with high water content. We believe that this generated the high porosity values in nonsterile microcosms with plants.

Table 1. Profiles of detritus (excludes sand), sand and porosity at different sediment depths

Depth (cm)	Sterile without plants			Nonsterile without plants			Nonsterile with plants		
	Detritus (g/L)	Sand (g/L)	Porosity	Detritus (g/L)	Sand (g/L)	Porosity	Detritus (g/L)	Sand (g/L)	Porosity
0.5	52.5	7.1	0.867	26.7	0.4	1.00	74.3	297.7	0.956
1.0	71.9	107.7	0.829	43.7	18.2	1.00	57.0	674.8	0.614
1.5	43.6	689.4	0.500	45.3	354.5	0.937	51.9	650.3	0.681
2.0	49.3	923.9	0.500	45.0	672.8	0.594	63.6	556.6	0.689
2.5	31.1	1,088.1	0.420	46.9	819.3	0.709	65.9	549.5	0.706
3.0	10.9	1,105.3	0.483	48.1	982.2	0.678	74.1	635.5	0.642
3.5	48.8	1,089.3	0.400	42.5	966.0	0.760	72.5	544.2	0.717
4.0	51.6	1,344.6	0.462	51.2	938.9	0.619	92.8	223.1	1.000
4.5	62.3	1,392.9	0.465	53.4	779.8	0.640	91.2	191.9	1.000
5.0	56.0	1,386.2	0.511	66.9	783.2	0.714	106.6	219.0	1.000
5.5	49.7	1,379.5	0.450	64.5	874.4	0.404	78.2	339.7	0.696
6.0	61.6	1,562.6	0.571	—[a]	—[a]	—[a]	78.6	409.9	0.874
6.5	59.8	1,367.2	0.484	—[a]	—[a]	—[a]	69.6	257.1	1.000
7.0	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	87.4	395.2	0.845

[a]No sediment layer. Total depth of sediment cores was not identical.

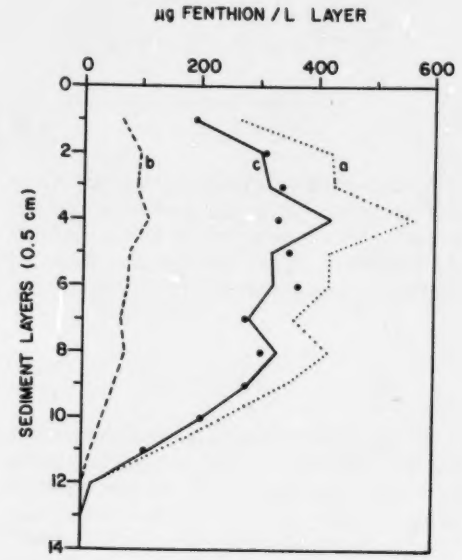

Fig. 5. Observed (circles) and predicted concentrations of fenthion in nonsterile sediments without plants. Model predictions of fenthion distribution using input data in Table 3 were based on three adjustments in the sediment biodegradation rate constant: (a) zero biodegradation; (b) biodegradation throughout the sediment; (c) model prediction with 7 mm sediment involved in biodegradation.

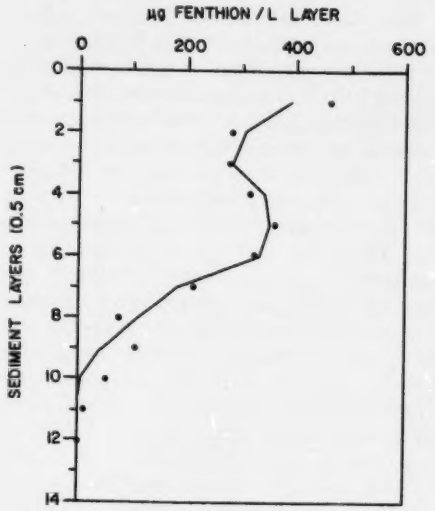

Fig. 6. Observed (circles) and predicted concentrations (solid line) of fenthion in the sediment of a nonsterile microcosm with plants. Model input data are listed in Table 3.

DISCUSSION

Loss of fenthion from the water column in nonsterile microcosms with and without plants was significantly greater than observed in the sterile microcosm, suggesting that fenthion can be biodegraded. Eichelberger and Lichtenberg [18] demonstrated that fenthion added to distilled water was unchanged over three weeks, but fenthion in raw river water decreased by half after one week, indicating possible biological degradation. Cripe et al. [17] reported that fenthion disappeared slowly (half-life ≥ 14 d) in shake flasks containing water from several Gulf Coast salt marshes, but degraded rapidly in the presence of sediment. Comparisons with half-lives from sterilized sediment tests indicated that the effect is due to the biotic component associated with the sediment.

Table 2. Observed and model-predicted fenthion budgets in microcosms; each microcosm was amended with 500 µg fenthion

	Fenthion (µg)							
	Sterile without plants		Nonsterile without plants				Nonsterile with plants	
Sources	Observed	Model	Observed	Model			Observed	Model
Sediment	203	195	204	268[a]	50[b]	207[c]	164	157[d]
Water	125	150	9	35[a]	15[b]	26[c]	7	13[d]
Total	328	345	213	303[a]	65[b]	233[c]	171	170[d]

[a]Model prediction with no biodegradation in the sediment.
[b]Model prediction with biodegradation constant throughout the sediment.
[c]Model prediction with 7 mm sediment involved in biodegradation.
[d]Model prediction with 1 mm sediment involved in biodegradation.

The fenthion added to the microcosms is subject to various transport and reaction processes including hydrolysis, photolysis, sorption, biodegradation and diffusion into the sediment. To assess the role of biodegradation as a loss mechanism in the nonsterile microcosms, each of the fate processes must be taken into account. Standard shake-flask tests were used to establish the kinetics of the abiotic fate processes: photolysis, hydrolysis and sorption. These tests and the results obtained are discussed in a companion paper [17]. Briefly, photolysis and hydrolysis were found to conform to first-order kinetics. Sorption to sediment was rapid and adequately described by a linear partition coefficient. The total abiotic degradation rate constant was found to increase with the addition of sediment to the shake flask. A linear increase was observed up to a sediment concentration of about 5 g/L. Values of the rate constants and the partition coefficient are given in Table 3.

The applicability of the shake-flask results to the microcosm systems was evaluated by comparing the observed concentrations to values computed from mass balance equations describing the fate of fenthion in the microcosm. These equations form a model of the microcosm that has been applied previously to the fate of Kepone [20]. The equation describing total chemical (dissolved + adsorbed) concentration in the water column is:

$$V_1 \frac{dc_{t_1}}{dt} = Qc_i - Qc_{t_1} + E_{1,2}(f_{d_2} c_{t_2} - f_{d_1} c_{t_1}) - (k_p + k_h + k_b) f_{d_1} c_{t_1} \quad (1)$$

where the subscripts 1 and 2 designate the water column and the top layer of sediment, respectively; V_1 is the water volume (in liters); c_t is the total concentration of toxicant (μg/L of segment volume); Q is the flow rate (L/h), which is zero in this case; c_i is the inflow toxicant concentration; $E_{1,2}$ is the exchange coefficient (L/h) between the water column and the interstitial water of the top sediment layer; f_d is the fraction of the total concentration of the chemical that is dissolved; k_p is the photolysis rate constant (h^{-1}); k_h is the hydrolysis rate constant (h^{-1}); and k_b is the biodegradation rate constant (h^{-1}). The exchange coefficient is the product of the diffusion coefficient and the sediment surface area divided by the length between the centroids of the water column and the top sediment layer. The equation for each sediment layer has the following form:

$$V_n \frac{dc_{t_n}}{dt} = E_{n-1,n}(f_{d_{n-1}} c_{t_{n-1}} - f_{d_n} c_{t_n}) - E_{n,n+1}(f_{d_n} c_{t_n} - f_{d_{n+1}} c_{t_{n+1}}) - (k_a + k_b) f_{d_n} c_{t_n} \quad (2)$$

where k_a is the total abiotic degradation rate. In these equations, the fraction of total chemical that is dissolved is computed from the sorption partition coefficient (K_p), the concentration of sediment (m) and the porosity of the bed (Φ):

$$f_d = \frac{1}{\Phi + K_p m} \quad (3)$$

In applying the model to the sterile microcosm, the shake-flask rate constants and partition coefficient were used and the sediment was separated into fourteen 0.5-cm layers. The maximum concentration of sediment contributing to detritus-mediated abiotic degradation (9 g/L) and diffusion coefficients were established by calibration of the model to the observed water column and sediment fenthion concentrations. The model was able to describe both the temporal distribution of fenthion in the water column (Fig. 1) and the spatial distribution of fenthion in the sediment at the end of the experiment (Fig. 4). The rate constant values and diffusion coefficients used in the model are given in Table 3. The diffusion coefficient values are consistent with those obtained in the Kepone study [20]. The relatively high diffusion coefficients between the water column and the first sediment layer is attributed to pore water mixing enhanced by turbulence from water column mixing [21,22].

We conclude from the comparison of the model with the observed data that the rate constants obtained in the shake-flask study are applicable to the microcosms. The computed and observed concentration results were in agreement after the calibration of diffusion coefficients whose actual values are unknown. If the reaction rate constants had been incorrectly specified, it would not have been possible to achieve such agreement. No matter what the diffusion rates are, the change in mass of fenthion in the microcosm is controlled entirely by the loss-rate mechanisms.

Comparison of the concentration of fenthion at different depths of sediment in sterile and nonsterile microcosms reveals that considerably more chemical reached the lower sediment depths in the nonsterile microcosms. If biodegradation occurs at these lower sediment depths, it is slow enough,

Table 3. Model input data

	Sterile microcosms	Nonsterile microcosms	
	Without plants	Without plants	With plants
Sediment layers	Fenthion diffusion rates (cm/sec^2 [$\times 10^{-5}$])		
Water → 1	41.0	100.0	100.0
1 → 2	1.0	72.0	72.0
2 → 3	1.0	72.0	72.0
3 → 4	1.0	72.0	72.0
4 → 5	1.0	72.0	72.0
5 → 6	1.0	72.0	10.0
6 → 7	1.0	72.0	5.0
7 → 8	1.0	72.0	5.0
8 → 9	1.0	10.0	5.0
9 → 10	1.0	5.0	1.0
10 → 11	1.0	5.0	1.0
11 → 12	1.0	1.0	1.0
12 → 13	1.0	1.0	1.0
13 → 14	1.0	1.0	1.0
Starting fenthion concn. ($\mu g/L$)	200	200	200
Partition coefficient ($\mu g/kg[\mu g/L]^{-1}$)	700[a]	700[a]	700[a]
Photolysis rate constant (h^{-1})	0.00072[a]	0.0013[a]	0.0013[a]
Hydrolysis rate constant in water (h^{-1})	0.00011[a]	0.00011[a]	0.00011[a]
Hydrolysis rate constant in sediment ($[h \cdot g]^{-1}$)	0.00023[a]	0.00023[a]	0.00023[a]
Biodegradation rate constant in water (h^{-1})	0	0.00061[a]	0.011[a]
Adjusted biodegradation rate constant ($[h \cdot g]^{-1}$) in sediment layer:			
1	0	0.0055	0.0011
2	0	0.0022	0
3 through 14	0	0	0
Maximum concentration of sediment contributing to detritus-mediated abiotic degradation (g/L)	9.0	9.0	9.0
Maximum concentration of sediment contributing to detritus-mediated biodegradation (g/L)	0	2.5[a]	2.5[a]

[a]From flask studies [17].

compared to its movement through sediment, to allow fenthion to accumulate. A biological factor, therefore, must transport fenthion physically within the sediment. Bioturbation from worm burrowing and feeding activities could explain the fenthion distribution in nonsterile microcosms. Large numbers of benthic organisms are not necessary for extensive sediment reworking [23], and burrowing organisms are responsible for lateral and vertical movement of sediment, interstitial water, dissolved gases [15,24–26] and the biological transport of organic chemicals [23].

Duursma and Gross [24] suggested that pore water mixing as a result of biological activity can be treated as a diffusive process, and a biological diffusion coefficient can be calculated. Bioturbation was also assumed to override turbulence and molecular weight influences, as discussed by Berner [27]. In addition, Duursma and Gross [24] reported that vertical transport by benthic invertebrates was several orders of magnitude greater than rates of molecular diffusion influx.

Benthic organisms facilitate movement of chemicals by accelerating diffusion and transporting compounds sorbed to sediment particles [23–25]. Therefore, diffusion rates in our model were increased (for predicting distribution of fenthion in nonsterile microcosms) until the calculated concentrations of fenthion in deeper sediment layers (through layer 11) were approximately equal to the observed concentrations. Below the 11th layer, fenthion concentrations were much lower, suggesting a great reduction in invertebrate activity. Therefore, diffusion rates calculated from the sterile microcosm were used in our model below the 11th sediment layer in the nonsterile microcosm without plants (Table 3, sediment layers 11 through 14). The diffusion rates recorded in Table 3 produced concentrations of fenthion predicted by our mathematical model that qualitatively described the observed gradient of fenthion concentrations with sediment depth.

Effects of biodegradation on both dissolved and sorbed chemical were evaluated in nonsterile microcosms with our mathematical model. Biodegradation of fenthion in sediment was directly related to the concentration of detritus. Sand as compared to detritus was assumed to have an insignificant number of attached microorganisms that could degrade fenthion. Since the quantity of detritus in each sediment layer was known (Table 1), adjustments in the biodegradation rate with depth could be calculated by the model. The maximum concentration of sediment contributing to detritus-mediated biodegradation (Table 3) was derived from shake-flask studies.

Bioturbation explains the mechanism for distributing fenthion to greater depths in the nonsterile microcosms as compared to the sterile microcosm, but does not account for the persistence of fenthion after 190 h given the high detritus-mediated degradation rate constant. Biodegradation probably does not occur below the sediment surface (>1 cm) because of oxygen-limiting conditions. Cripe et al. [17] have shown in shake-flask tests that fenthion does not biodegrade in low oxygen (nitrogen purged) conditions. If biodegradation did not occur in the sediment, the model overestimated fenthion concentrations in the sediment (Fig. 5, curve a). If biodegradation occurred throughout the sediment, the model underestimated observed data (Fig. 5, curve b). The best estimation was obtained when the model confined biodegradation to the top 7 mm of sediment and reduced biodegradation to zero below 7 mm (Fig. 5, curve c). This is supported by Novitsky's findings [28,29] that high sediment microbial activity is present at the sediment–water interface. Changes in the depth where biodegradation occurred in sediment had minimal effects on water concentration (Fig. 2, curves a, b, and c).

When model parameters identical to nonsterile microcosm without plants were used for the nonsterile microcosm with plants, the predicted fenthion concentration in water was higher than observed values. This was anticipated because plants provide surfaces for microbial attachment that could support a large microbial biomass [6,7]. Gallagher et al. [11] found that microorganisms increased in biomass as a response to organic material leached from *Spartina alterniflora* leaves. In earlier shake-flask studies [17] the presence of *Spartina alterniflora* produced a substantially higher fenthion degradation rate constant (Table 3). Because only approximately 1% of the total fenthion added was recovered from the plants, we concluded that the enhanced loss of fenthion from the water was due to biological degradation and not just sorption/assimilation storage phenomena.

The choice of diffusion rates for the nonsterile microcosm with plants was based on rates calculated for the nonsterile microcosm without plants (Table 3) and the budget for the observed distribution of fenthion (Table 2). The best estimation of the mathematical model to the observed fenthion distribution in water (Fig. 3) and sediment (Fig. 6) was obtained with diffusion rates shown in Table 3. The diffusion rates in the nonsterile microcosm with plants were greatly reduced at layer 4, whereas in the nonsterile microcosm without plants, the diffusion rates decreased at sediment layer 7. The presence of plant roots may have been a physical barrier to movement of fenthion to lower sediment depths. The best estimation of the model to observed fenthion concentrations in the nonsterile microcosm with plants occurred when biodegradation in the sediment was limited to the top 1 mm of sediment and was reduced to zero below the 1 mm depth in the sediment. Although differences occurred in biodegradation rates in water and movement within

the sediment, there was no significant difference in fenthion loss from the water column between nonsterile microcosms with and without plants.

CONCLUSIONS

The assessment of biodegradation rates of xenobiotic chemicals in the natural sediments is a complicated process. Although the microcosms appear to be an excellent method for carrying out these assessments, our work indicates the importance of a thorough knowledge of all relevant fate processes in these systems. Our study emphasizes the importance of biodegradation in sediment, bioturbation, and the presence of plants in the distribution and persistence of fenthion in microcosms:

1. Biodegradation of fenthion appeared restricted to the upper sediment layers possibly due to oxygen limitations. Biodegradation was not linear with respect to sediment concentration beyond 2.5 g of detritus per liter.
2. Fenthion was transported much deeper into the sediment in nonsterile microcosms, possibly by benthic invertebrates, as compared to the sterile microcosm.
3. The presence of plants seemed to increase the loss of fenthion from water and limit the depth that fenthion was distributed in the sediment.
4. Abiotic and biotic degradation information derived from flask studies in conjunction with the mass balance mathematical model was sufficient to predict observed microcosm data.

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